

Electrolytes for Li-Ion Cells in Low Temperature Applications

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ABSTRACT

Prototype AA-size lithium-ion cells have been demonstrated to operate effectively at temperatures as low as -30 to -40°C. These improvements in low temperature cell performance have been realized by the incorporation of **ethylene carbonate**-based electrolytes which possess low melting, low viscosity **co-solvents**, such as methyl acetate, ethyl acetate, γ -butyrolactone, and ethyl methyl carbonate. The cells containing a 0.75M LiPF₆ EC+DEC+DMC+EMC (1:1:1:1) electrolyte displayed the best performance at -30°C (> 90% of the room temperature capacity @ ~C/15 rate), whereas, at -40°C the cells with the 0.75M LiPF₆ EC+DEC+DMC+MA (1:1:1:1) and 0.75M LiPF₆ EC+DEC+DMC+EA (1:1:1:1) electrolytes showed superior performance.

Introduction

A number of upcoming NASA missions require **energy storage** devices which display **high energy density** and can effectively operate at low temperatures. **Lithium-ion batteries** have been identified as the most promising technology which can meet these stringent requirements. Some of the future NASA applications for which lithium-ion batteries have been baselined include the Mars 2001 Lander and the Mars 2003 Sample Return/Athena Rover, the requirements of which are elaborated upon in our companion paper¹. These applications generally require operation to temperatures as low as -30 °C, at moderate rates of charge and discharge. Previously, the state-of-art lithium-ion cell technology has been limited to operating temperature ranges of -10° to +40°C. Due to improvements which have been realized through electrolyte modifications, better low temperature performance of lithium-ion cells has been demonstrated to temperatures as low as -30°C.^{2,3,4} Although these improvements are substantial, there is continued interest to develop lithium-ion cells which are capable of performance at extremely low temperatures (-40 to -60°C) and

have improved rate capability at more moderate temperatures (-30 to -10°C).

To enable the operation of lithium-ion cells at these very low temperatures, we have been engaged in the further development of advanced low temperature electrolytes under sponsorship of the Mars Exploration Program. In this paper we would like to report the low temperature performance characteristics a number of ethylene carbonate-based electrolytes to which appropriate co-solvents, such as methyl acetate, ethyl acetate, γ -butyrolactone, and ethyl methyl carbonate, are added to sufficiently lower the viscosity and melting point of the solution. The investigation of these electrolytes has included their incorporation into AA-size prototype cells (fabricated by Wilson Greatbatch Ltd. according to JPL design), and experimental half-cells. In addition, conductivity measurements of a number of formulations have been performed.

Experimental

The specific conductivity of a number of electrolyte solutions was measured over the temperature range of -60°C to 25°C. This was accomplished by using a conductivity cell which

consists of two platinized platinum electrodes which are immobilized in a glass apparatus and separated by a fixed distance. The temperature was controlled in these experiments by utilizing a Tenney environmental low temperature chamber ($\pm 1^\circ\text{C}$).

The candidate electrolytes were evaluated in AA size prototype cells fabricated by Wilson Greatbatch Ltd. (Greatneck, New York) according to JPL design and containing materials prepared by JPL. These cells were fabricated with LiCoO_2 as the cathode material and MCMB carbon as the anode material. These cells were evaluated for rate capability, low temperature performance and cycle life. All electrolytes were of battery-grade purity. Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat (and Solartron 1255 Frequency Response Analyzer for impedance measurements) interfaced with an IBM PC, using Softcorr 352 (and M388 for impedance) software. Cycling data were collected using an Arbin battery test system.

Results and Discussion

In designing electrolytes which possess high conductivity at low temperatures, the solutions should possess a combination of several critical properties, such as: a high dielectric constant, low viscosity, adequate coordination behavior, as well as the appropriate liquid ranges and salt solubilities in the medium. Additionally, in the selection of an electrolyte system it is crucial to consider its compatibility with the cell chemistry in terms of stability. It has been observed that the nature of the surface films formed on the carbon electrodes can dramatically impact the low temperature performance of lithium-ion cells, often offsetting the advantages of high electrolyte conductivity.

Electrolyte Conductivity

A number of carbonate-based electrolytes containing low viscosity, low melting additives have been prepared and the conductivity measured over a temperature range of -60°C to 25°C . The electrolytes assessed consisted of baseline formulations, 1.0M LiPF_6 EC + DEC + DMC (1:1:1), to which the low viscosity co-solvents were

added, including: methyl formate (MF), methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), ethyl butyrate (EB), and γ -butyrolactone (GBL). Of the electrolytes investigated, the quaternary formulations that displayed the highest conductivity at low temperatures were ones containing the lower molecular weight formates and acetates and displayed the following trend: $\text{MF} > \text{MA} > \text{EA} > \text{EP} > \text{GBL} > \text{EB}$. The conductivity values for these quaternary solutions are shown in Fig. 1.

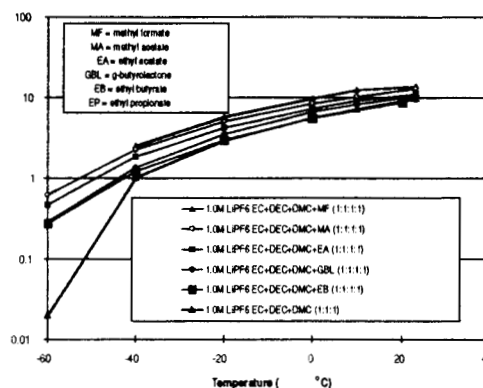


Fig. 1. Specific conductivity of EC-based quaternary solvent electrolyte systems from 25 to -60°C .

Prototype AA-Size Lithium-Ion Cells

A number of prototype AA-size lithium-ion cells were fabricated to investigate the effect of electrolyte type upon the low temperature performance. The electrolytes chosen for evaluation are listed in Table 1, along with the corresponding reversible and irreversible capacities observed after the first formation cycle. The electrolytes selected for evaluation have also been investigated in lithium-carbon three electrode half-cells⁶ in an attempt to characterize the nature of the surface films formed on carbon, although their full discussion is beyond the scope of this paper.

Electrolyte Type	Reversible Capacity (Ah/g)	Irreversible Capacity (Ah/g)
0.75M LiPF ₆ EC+DEC+DMC+MA (1:1:1:1)	0.377	0.051
0.75M LiPF ₆ EC+DEC+DMC+GBL (1:1:1:1)	0.315	0.071
0.75M LiPF ₆ EC+DEC+DMC+EM C (1:1:1:1)	0.366	0.071
0.75M LiPF ₆ EC+DEC+DMC+EA (1:1:1:1)	0.351	0.085
0.75M LiPF ₆ EC+DMC+MA (1:1:1)	0.354	0.081

Table. 1. Reversible and irreversible capacities of AA-Size lithium-ion cells after the first formation cycle.

Discharge Capacity at Low Temperatures

The discharge capacities of the cells were evaluated over a temperature range of -40° to 23°C and at a number of different charge and discharge rates. When the cells were charged at room temperature and discharged at low temperature (-30°C) good capacity was realized in many cases. The cell containing the quaternary ethylmethyl carbonate (EMC)-based electrolyte displayed the best capacity, as shown in Fig. 2. The ethyl acetate and methyl acetate-based systems also showed good performance, whereas the GBL-containing cells delivered low capacity.

When the discharge capacity delivered by the cell containing the electrolyte 0.75M LiPF₆ EC+DEC+DMC+EMC (1:1:1:1) is compared as a function of temperature, as shown in Fig. 3., the excellent low temperature characteristics are

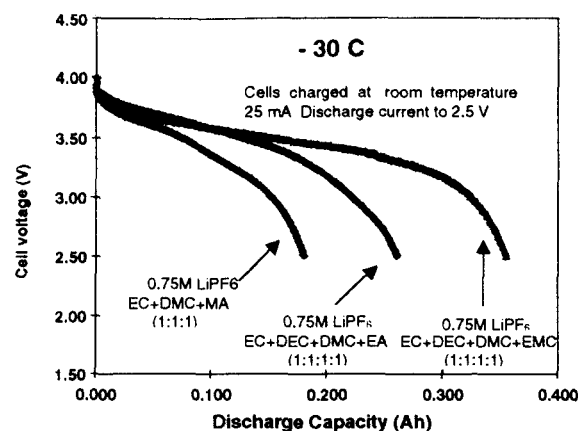


Fig. 2. Discharge capacity of AA-size lithium-ion cells at -30°C. Cells were charged at room temperature and discharged at LT (discharge current = 25 mA (~C/15) to a 2.5 V cut-off).

illustrated. As shown, more than 90% of the room temperature capacity can be realized upon discharging at -30°C (~C/15 rate). This represents a significant improvement over the performance delivered in comparable AA-size graphite-LiCoO₂ lithium-ion cells with the baseline low temperature electrolyte (1.0M LiPF₆ EC+DEC+DMC (1:1:1)) investigated previously.

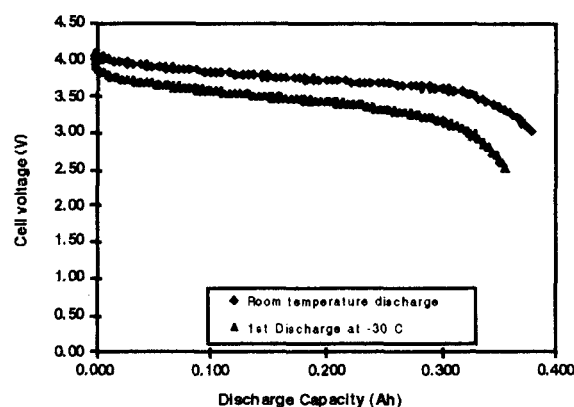


Fig. 3. Effect of temperature upon the discharge capacity delivered by a AA-size cell containing 0.75M LiPF₆ EC+DEC+DMC+EMC (1:1:1:1). The cell was charged at 25°C and discharged (25mA or ~C/15 rate) at various temperatures (25 and -30°C).

When the cells were charged at room temperature and discharged at -40°C (after approximately a 4 hour equilibration period), as illustrated in Fig. 4, excellent discharge capacity was delivered in some cases. The cell possessing the ethyl acetate-containing electrolyte was observed to display the best performance with $> 140\text{ mAh}$ being delivered at -40°C , which corresponds to greater than 35% of the room temperature capacity. Although excellent capacity was obtained with the $0.75\text{M LiPF}_6\text{ EC+DEC+DMC+EMC (1:1:1:1)}$ containing cell at -30°C , only negligible capacity was delivered at -40°C . This poor performance is most likely attributable to the high melting point of the all carbonate-mixture coupled with the low salt concentration employed. Although lower electrolyte salt concentrations result in higher conductivity at low temperatures due to lower solution viscosity, the freezing point depression effect is reduced leading to higher melting points. In contrast to ethylmethyl carbonate (m.p. = -14°C)⁷, methyl acetate and ethyl acetate have very low melting points (-98° and -84°C , respectively) producing highly conductive solutions at very low temperatures ($>-40^{\circ}\text{C}$) which translates into improved cell performance. As illustrated in Fig. 5, more than one-third of the room temperature capacity can be delivered by a cell containing $0.75\text{M LiPF}_6\text{ EC+DEC+DMC+EA (1:1:1:1)}$ at -40°C at moderate rates.

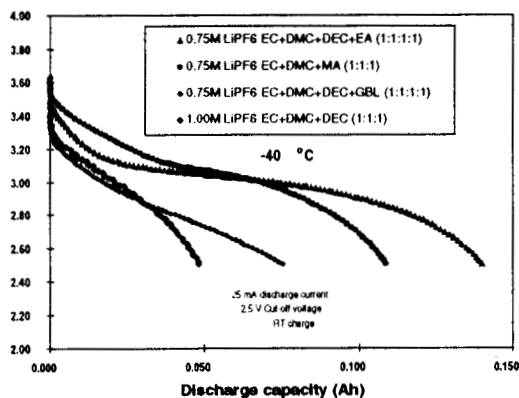


Fig. 4. Discharge capacity of AA-Size lithium-ion cells at -40°C . Cells were charged at room temperature and discharged at LT (discharge current = 25 mA ($\sim\text{C}/15$) to a 2.5 V cut-off).

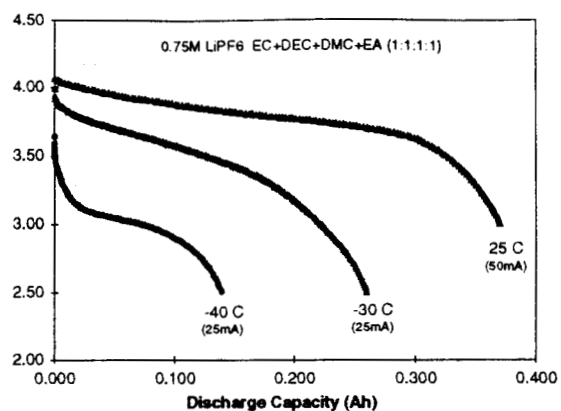


Fig. 5. Discharge capacity of a AA-size lithium-ion cell at various temperatures. Discharge current = 25 mA ($\sim\text{C}/15$) to a 2.5 V cut-off.

Charge Acceptance at Low Temperatures

When cell performance was evaluated at low temperatures ($>-20^{\circ}\text{C}$), it was generally observed that the charge process is less facile than the discharge process resulting in lower capacities when cycled continuously at low temperature. The relative charge acceptance at low temperatures is most likely governed largely by the nature of the SEI film on the carbon surface, which has been shown to be dependent upon the electrolyte type. The slower kinetics of lithium intercalation at low temperature imply that the charge acceptance characteristics of cells define the performance. In some cases, only half of the discharge capacity is delivered when the cell is charged at low temperature compared with a room temperature charge, as shown in Fig. 6.

The poor performance of the acetate-containing cells upon cycling at low temperature is due to the inability to effectively charge them at temperatures of -30°C and below, even if low rates are employed ($>\text{C}/25$), as shown in Fig. 7.

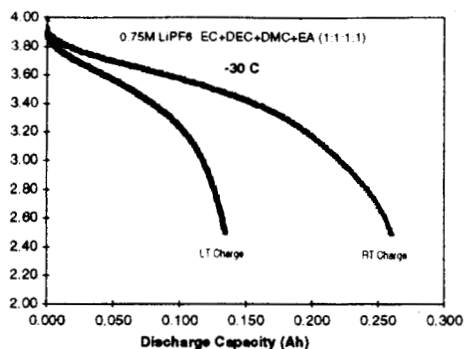


Fig. 6. Discharge capacity of AA-Size lithium-ion cells at -40°C . Cells were charged at room temperature and discharged at LT (discharge current = 25 mA ($\sim\text{C}/16$) to a 2.5 V cut-off).

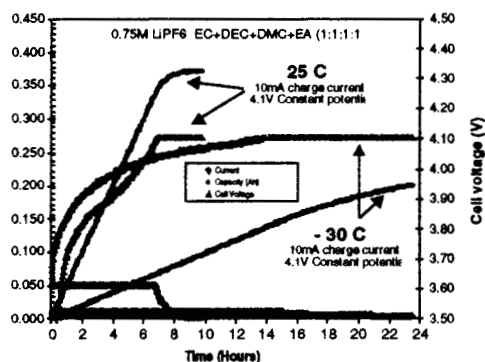


Fig. 7. Charge acceptance of AA-Size lithium-ion cells at room temperature and at -30°C .

Cycle Life Performance at Low Temperatures

In addition to evaluating the cells in terms of the rate capability as a function of temperature, the low temperature cycle life was evaluated at -20 and -40°C . As shown in Fig. 8., when the cells were cycled at -20°C the best performance was obtained with the acetate containing electrolyte cells, which correlates well with the observed high conductivity of these electrolytes.

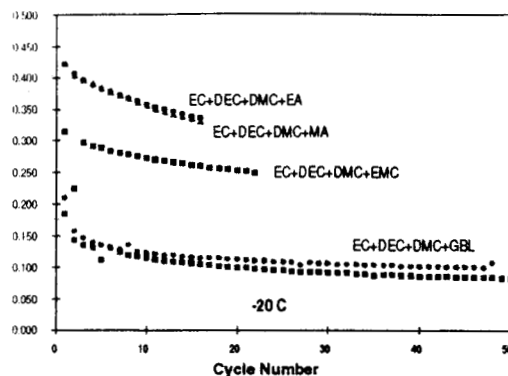


Fig. 8. Cycle life performance of AA-size cells at -20°C (25 mA charge and discharge current ($\sim\text{C}/15$)).

When the cells were cycled at -40°C , modest capacity was delivered (~ 60 mAh) by the ethyl acetate-containing cell after prolonged cycling at a moderate rate ($\text{C}/15$).

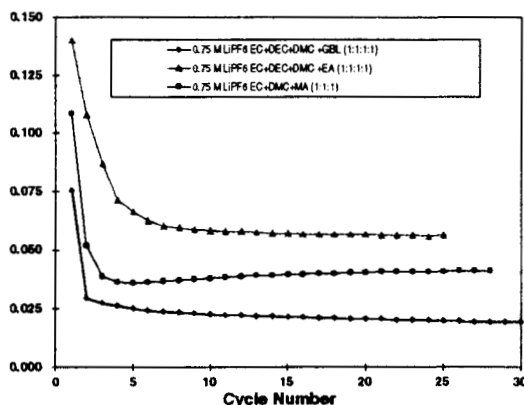


Fig. 9. Cycle life performance of AA-Size lithium-ion cells at -40°C . Cells were charged and discharged at LT (25 mA discharge current ($\sim\text{C}/15$) to 2.5 V cut-off).

Electrochemical Impedance Spectroscopy

In addition to evaluating the electrical performance of the AA-size cells, a.c. impedance measurements were also taken to gain a greater

understanding of the effect of electrolytes upon the low temperature performance of lithium-ion cells. When the impedance spectra of a number of cells are compared, as shown in Fig. 10, it is evident that the series resistivity (or solution resistance), R_s , correlates well with the observed conductivity trends. The polarization resistance associated with the nature of lithium diffusion and charge transfer processes at the electrode, however, appear to reflect the relative reactivity of the electrolyte and the morphology of the SEI film deposited.

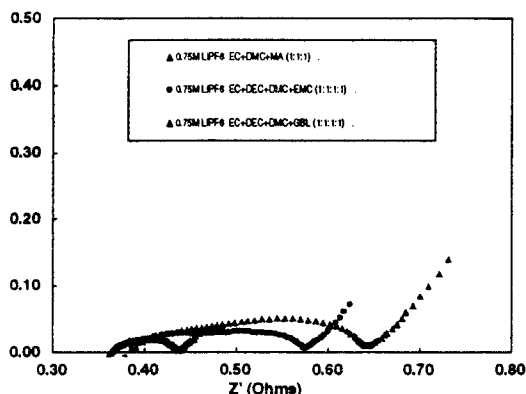


Fig. 10. EIS of AA-Size lithium-ion cells at room temperature after formation cycles. Cells were in a full state of charge.

Conclusions

A number of electrolytes based on ternary and quaternary mixtures of organic carbonates to which solvents possessing low viscosity and low melting points are added, such as, MA, EA, GBL, and EMC, have been demonstrated to result in improved low temperature cell performance. At -30°C , the quaternary formulation containing EMC displayed the best performance, whereas at -40°C the acetate containing cells delivered the most capacity.

References

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Acknowledgments

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